SEASONAL PHOSDRIN DEGRADATION ON ROW CROPS IN MONTEREY COUNTY, 1990

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ABSTRACT

In June and October, 1990, the California Department of Food and Agriculture (CDFA), Worker Health and Safety Branch, monitored 23 vegetable crop fields in Monterey County to characterize seasonal variation in mevinphos (Phosdrin[R] 4 EC, EPA reg. no. 5481-412-AA) degradation. The reentry interval for mevinphos is two days (15). Fields were sampled for four days post-application, according to the method of Gunther et al. (3, 4). Foliage samples were extracted in the field, frozen and sent to the Chemistry Services Laboratory in Sacramento for analysis of the E and Z (alpha and beta) isomers of mevinphos. The quantity of each isomer was summed and linear regression was performed on the natural log of the total dislodgeable mevinphos residues for each field. The mean half-life for all crops was 24 $\pm$ 10 hours in June (n = 13 fields) and 18 $\pm$ 8 hours in October (n = 10 fields). There was no significant difference between these means ($p>0.05$), indicating there was no marked seasonal effect on dissipation rate.

INTRODUCTION

Characterization of residue dissipation of acutely toxic, short-lived organophosphate insecticides such as mevinphos calls for surveying degradation under various field and seasonal conditions since differences in these parameters can contribute to variations in the rate of pesticide residue degradation (5). If seasonal effects cause residues to decay more slowly, the reentry interval may need to be reevaluated. In a previous CDFA study, methomyl, a carbamate insecticide, was found to exhibit seasonally related dissipative behavior with an increase in half-life with the progression of summer months (12). The findings prompted regulation requiring an extended reentry interval later in the season. It was speculated that the cooler weather conditions and shorter day length in the fall increase the possibility of slower mevinphos degradation. In previous investigations, half-lives of 9-34 hours were calculated for mevinphos on strawberries, lettuce, cauliflower and Chinese cabbage, with a mean half-life of 18$\pm$ 9 hours for all previous studies combined (6, 7, 8, 9, 10, 11). This study investigated the degradation of mevinphos on lettuce, cauliflower, celery and green onions in the summer and lettuce, broccoli, cauliflower and celery in the fall. The residue data were analyzed to determine any seasonal effects on the half-life of mevinphos and compared to dissipation rate estimates from previous studies.

MATERIALS AND METHODS

With the assistance of pest control operators in Monterey County, 23 fields were selected and monitored for four days. Five crops, all normally hand harvested, were monitored as follows: 15 lettuce fields (7 head lettuce, 3 butter, 3 Romaine, 2 red leaf and 1 green leaf), 3 cauliflower, 3 celery, 1 broccoli and 1 green onion. All June applications were made by helicopter. October applications were by either helicopter or ground rig. June temperatures ranged from 52 - 70^{o} F during the course of the study and October temperatures ranged from 52 - 60^{o} F. Mevinphos was applied at either 0.25, 0.38 or 0.5 pounds a. i. (active ingredient) per acre. Fields were chosen and sampled using the method developed by Gunther et al. (3, 4), and the guidelines of Blewett et al. (1). Four foliage samples were taken in each field. For lettuce, cauliflower and broccoli, each sample consisted of 40 leaf disks taken with a 2.54 cm diameter leaf punch from a marked 20-meter portion of one row. Two leaf disk punches were taken per plant. For green onions, 40 one-inch leaf strips were cut with the punch and for celery, 20 whole leaves were collected per sample. The surface area was determined by measurement on a surface area meter after residue extraction. All samples were placed in four-ounce glass jars, sealed with aluminum foil, capped, and kept on ice until extraction. The first post-application samples were collected at least 2 hours and no later than 24 hours after application. Initial sampling times varied due to distances between fields and deviations from scheduled application times. Subsequent sampling was conducted at 24, 48, 72 and 96 hours post- application, unless fields were impassable due to irrigation.

Sample Analysis Samples were prepared according to Gunther et al. (3, 4), and analyzed for the presence of the E and Z isomers of mevinphos. Since mevinphos is highly volatile and dissipates quickly, field extraction of the foliage samples was begun within one hour of collection (14). Refrigerated and frozen storage stability of mevinphos had been previously determined to be essentially quantitative (95-100% recovery) after zero, three, four and six days' storage (2). Samples were rotated three times on a mechanical roller (20, 20 and 10 minutes each) with 50 mL of 1% surfactant, sodium dioctyl sulfosuccinate. After each shaking, the extracts were poured into 25-mL polyethylene bottles, capped, then frozen until isomer extraction and analysis was completed by CDFA Chemistry Services Laboratory. The aqueous samples were extracted twice with 50 mL ethyl acetate which was then dried by the addition of anhydrous sodium sulfate. After volume reduction the extracts were analyzed by gas liquid chromatography on a Hewlett-Packard 5880A chromatograph equipped with a nitrogen-phosphorus detector. The chromatographic conditions were: column, 10 m x 0.53 mm HP 20M Carbowax^R; carrier gas (He), 10 mL/min; H_2, 5 mL/min; air, 160 mL/min; make-up gas (He) 10 mL/min; injector temperature, 250^o C; column temperature, 150^o C isothermal; and detector temperature, 250^o C. The retention time using the above conditions was 2.18 minutes for the E isomer and 2.55 minutes for the Z isomer. The minimum detectable level for both the E and Z isomers was 0.5 micrograms per sample.

Data Analysis The residues of the E and Z isomer were summed for total dislodgeable mevinphos (ug/cm^2) for each field and sampling interval. Green onion and celery residues were divided by the mean surface area per sample. Data were analyzed within and between seasons using linear least squares regression on the natural log of the total residues versus time post-application (13). Half-life data were rounded to the nearest hour. A 0.05 level of statistical significance was selected. Comparisons were made between residue behavior for all crops for each season, for each crop by application rate within each season and for the same crops and application rates between seasons.

RESULTS

Raw data (total dislodgeable mevinphos residues) are presented in Appendices I-V. Table I presents the crops, month monitored, application rate and method, length of sampling interval, calculated half-life of mevinphos, level of statistical significance of the regression and the range of values for the coefficients of determination (r^2) for each regression. Twenty-two of the 23 regressions were significant, the exception being one October lettuce field. Not all crops were treated with mevinphos during each seasonal monitoring period, thus reducing the number of analogous seasonal residue comparisons. The half-life for fields sampled in June ranged from 10 to 50 hours and, in October, from 15 to 20 hours. The mean mevinphos half-lives were similar for summer and fall (24$\pm$10 hours, (n=13 fields), vs. 18 $\pm$ 8 hours (n=10 fields), for June and October, respectively) and did not differ significantly. The greater variation for the June data is likely due to a range in initial sampling interval of 4 - 24 hours, compared to October, when initial sampling ranged from 2 - 12 hours after application. The initial sampling intervals for lettuce differed by only eight hours between the seasons and the data gave nearly identical half-lives for June and October (22$\pm$6 hours (n=9 fields) and 20 $\pm$ 11 hours (n=6 fields), respectively). The slowest decay was observed in June on cauliflower (half-life=50 hours) and differed significantly from the decay rate in October (half-life=18 hours). Green onions in June exhibited the most rapid decay (half-life = 10 hours).

Table II compares the regressions for similar crops and application rates during June and October and Figures 1-3 present the regression lines. Coefficients of determination (r^2) ranged from 0.15 - 0.84. For these crops (lettuce at 0.25 lb a.i./acre, cauliflower at 0.5

lba.i./acre and celery at 0.25 lb a.i./acre) all June applications were by helicopter and all October applications were by ground rig. Overall, there was no significant difference in decay rate between June and October although higher residues were found for June. In individual crop comparisons, no difference in decay rate was found for lettuce while significantly higher mean residues were found for June. For cauliflower and celery, both decay rates and residue levels differed significantly by season. However, the effect cannot be attributed to seasonal parameters since the application method differed.

DISCUSSION AND CONCLUSIONS

Mevinphos' efficacy and rapid dissipation make it very useful for crops requiring a quick insect "clean-up" before harvest. This organophosphorous insecticide has extreme acute toxicity. Margins-of-safety for harvesters will be determined, in part, by the magnitude of dislodgeable foliar residues. Since field workers contact treated foliage relatively soon after application, it is important to assess mevinphos' dissipation behavior under a range of actual use conditions. Differences in season, application method, rate, dilution and crop may influence the rate of pesticide decay (5, 12). It appears from this study that mevinphos does not exhibit a seasonal variation in dissipation behavior. In spite of the extreme hazard posed by mevinphos, this study reveals low risk to harvesters due to the low magnitude of the DFR and its rapid breakdown.

Comparisons of mevinphos degradation rate by crop within a season gave overall half-lives of 24 $\pm$ 10 hours for June and, for October, 18 $\pm$ 8 hours. These estimates do not differ significantly from the overall half-life of 18 $\pm$ 9 hours (range= 9-34 hours, n = 25 fields) calculated for lettuce, strawberries, cabbage and cauliflower from 6 previous investigations (6, 7, 8, 9, 10, 11). Initial sampling times in previous studies ranged from 1-8 hours and in the present study, from 2 - 24 hours post-application. While the estimates of decay rate are similar for the present study compared to the previous work, much of the June data is from fields sampled initially at 24 hours, at or after the expiration of the estimated first half-life. This may be related to the 30% longer half-life calculated for June compared to October and to previous investigations. Initial sampling should be conducted before expiration of the estimated first half-life of 18 hours post-application to obtain more detailed knowledge of mevinphos' fate under field conditions.

In comparing mevinphos degradation by crop between seasons, lettuce showed no significant difference between summer and fall. For celery and cauliflower, a significant difference was found, but it is not clear why the June applications resulted in significantly greater residues than the October applications. This phenomenon may be due to variations in plant maturity and application techniques. We were unable to locate both air and ground applications during June and October and comparison of these factors was not part of the study design.

Table I. Mevinphos half-life estimate and coefficients of determination (r^2 value) for five row crops in June and October, 1990, Monterey County

Month	n Fields	Crop	pounds a.i./ac	Method	Intervals (hrs)	Half-life (hrs$\pm$SD)	r^2 value
June	3	lettuce	0.25	air	4-96	19$\pm$2	0.86-0.88
	6	lettuce	0.38	air	4-96	24$\pm$7	0.55-0.86
	1	cauliflower	0.50	air	24-96	50	0.25
	2	celery	0.25	air	24-72	25$\pm$2	0.41-0.67
	1	gr. onion	0.25	air	24-96	10	0.66
October	6	lettuce	0.25	ground	12-48	20$\pm$11	0.1-0.67
	1	broccoli	0.25	air	4-96	15	0.85
	2	cauliflower	0.50	ground	2-96	18$\pm$1	0.90-0.92
	1	celery	0.25	ground	12-96	16	0.71
Total	23						

Table II. Results of regressions between ln(mevinphos residues) on similar crops during June and October, 1990, Monterey County

Crop	Month	pounds a.i./acre	n[a]	Slope	Intercept	r^2	Level of Signif. (p value)
Lettuce	June	0.25	133	-0.030	-2.72	0.55	$p>0.05$
	October	0.25	133	-0.032	-3.62	0.15	$p>0.05$
Cauliflower	June	0.50	50	-0.014	-1.19	0.54	$p<0.05$
	October	0.50	50	-0.039	-1.83	0.84	$p<0.05$
Celery	June	0.25	36	-0.022	-2.97	0.59	$p<0.05$
	October	0.25	36	-0.043	-2.60	0.75	$p<0.05$
All 3 Crops	June	-----	223	-0.023	-2.72	0.27	$p>0.05$
	October	-----	223	-0.032	-3.02	0.36	$p>0.05$

[a] number of residue values

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